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Surface enhanced Raman scattering from metallic nanoshells with nonlocal dielectric response

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Abstract

The Gersten–Nitzan model is applied to study the surface enhanced Raman scattering from a molecule adsorbed on a spherical metallic nanoshell. The nonlocal dielectric response from the nanoshell has been accounted for by using a phenomenological model. For a fixed outer radius of the shell, the enhancement ratio is calculated over a large range of scattering frequency and inner radius of the shell, including the case of a solid metallic particle. The effect due to different core materials is also studied. It is concluded that the nonlocal effects can be significant for very close molecule–shell distances, and for shells with very small sizes and/or thickness, leading to smaller enhancement in general. This can affect the plasmon resonances as well as the optimal shell thickness for the shell acting as a Raman enhancer.

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1. Introduction

Since its first fabrication in 1998 [1], the metallic nanoshell has been studied intensively in various imaging and spectroscopic applications, by employing the high tunability in its plasmon resonance frequency as well as the enhanced local fields in the vicinity of the nanoshell [2–9]. In particular, surface enhanced Raman scattering (SERS) from these nanoshell substrates has been studied systematically in several recent works published by the Halas group [2,6,9]. In these studies, SERS was observed from para-mercaptoaniline in either solutions containing these metallic nanoshells [2,6] or nanoshell thin film substrates [9], with enhancement at least as strong as those obtained from colloidal aggregates of metallic particles. Moreover, it was concluded that most of the enhancement features could be determined from the optical behavior of mutually independent nanoshells, unlike the case with colloidal particles where the aggregate nature of the substrate plays a significant role. Furthermore, SERS was achievable with infrared (IR) excitation frequencies (0.78 and 1.06 μm) using noble metal nanoshells, with the result depending crucially on the ratio of the inner and outer shell radii as well as the shell thickness.

The theoretical understanding of the above nanoshell SERS experiment has so far been largely based on the calculation of the surface fields at both the incident and scattered frequencies using the Mie theory [2,6,9,10]. Except for the very recent theory [10] based on the density matrix approach, the role of the molecular dipole has not been included in most of these previous analysis of the observed SERS spectrum. Furthermore, the optical response of the metallic shell has so far been limited to be described by classical bulk dielectric response functions in all the previous works. It is the purpose of the present communication to perform a more detailed model study of the phenomenon by calculating the Raman scattering cross section from a molecular dipole adsorbed on such a metallic nanoshell. Furthermore, we shall account partially for the quantum nature of the metallic electrons via a nonlocal dielectric response of the nanoshell, which will lead to significant modification of the classical electromagnetic (Mie) theory for shells of very small sizes and thickness. To this end we shall adopt the well-known semiclassical model of Gersten and Nitzan (GN) [11], which is adequate when both the shell size (b) and the molecule–shell distance (d) are small compared to the excitation wavelength.

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In addition, we are also interested in the comparison of the SERS signals obtainable from a nanoshell with those from the corresponding metal particles of the same external sizes. This will clarify, once and for all, how the two systems compare when acting as "SERS enhancers", as the previous experimenters seemed to have implied in their works [2,6,9].

2. Theoretical model

According to the GN model, the Raman cross section from a dipole-nanoshell system can be expressed in terms of the induced polarizability ($\Delta\alpha$) for the molecule due to the change of nuclear coordinate (Q) as follows [11]:

$$\sigma_{\text{RAMAN}} = \frac{8\pi}{3}\left(\frac{\omega}{c}\right)^4 (\Delta Q)^2 \left(\frac{\partial\alpha}{\partial Q}\right)^2 \times \left|\frac{1}{1-\alpha G_\perp}\left(1+\frac{2\alpha_1^S}{(b+d)^3}\right)\right|^4, \quad (1)$$

where α_ℓ^S is the ℓth-pole polarizability of the nanoshell given by [12]

$$\alpha_\ell^S = \frac{(\varepsilon-\varepsilon')\,\ell\,[\ell+\varepsilon\,(\ell+1)]\,a^{2\ell+1}+\ell\,(1-\varepsilon)\left[\varepsilon'\ell+\varepsilon\,(\ell+1)\right]b^{2\ell+1}}{(\varepsilon-\varepsilon')\,(\varepsilon-1)\,\ell\,(\ell+1)\,a^{2\ell+1}-(\varepsilon\ell+\ell+1)\left[\varepsilon'\ell+\varepsilon\,(\ell+1)\right]b^{2\ell+1}}\,b^{2\ell+1}, \quad (2)$$

and the "image-field factor" can be obtained as

$$G_\perp = \sum_\ell \alpha_\ell^S \frac{(\ell+1)^2}{(b+d)^{2\ell+4}}. \quad (3)$$

Note that we have assumed a nanoshell of dimension a (inner radius) and b (outer radius), and the molecular dipole is along the radial direction, which is known to give a maximum SERS signal [11]. We have also assumed the molecule to be placed in vacuum and that the shell is made of a metal of dielectric constant ε coated on a core of dielectric constant ε'. The enhancement ratio (R) is defined as the ratio of σ_{RAMAN} in Eq. (1) to the same quantity in the absence of the nanoshell. Hence we obtain

$$R = \left|\frac{1}{1-\alpha G_\perp}\left(1+\frac{2\alpha_1^S}{(b+d)^3}\right)\right|^4, \quad (4)$$

with α_1^S obtained from Eq. (2) by setting $\ell = 1$. To model the dispersive properties of the metal, we adopt the Drude model with modifications introduced to account for the additional damping due to electron scattering at the shell boundaries [13]:

$$\varepsilon(\omega) = 1+\varepsilon_\infty - \frac{\omega_P^2}{\omega\,(\omega+\mathrm{i}\Gamma)}, \quad (5)$$

where ε_∞ accounts for the contribution from core electrons and interband transitions, and the damping constant $\Gamma = \Gamma_b + \frac{Av_F}{(b-a)}$, with the bulk rate modified by the surface scattering term, where A is a geometrical factor of unity order of magnitude, and v_F is the Fermi velocity of the metal. To account for the nonlocal optical effects, we replace the polarizability in (2) by the following nonlocal polarizability of the metallic shell, which was worked out previously in the literature [12,14]:

$$\alpha_\ell = -\left(\frac{\ell\beta+b\gamma}{(\ell+1)\beta-b\gamma}\right)b^{2\ell+1} \equiv \Delta_\ell b^{2\ell+1}, \quad (6)$$

where the quantities β and γ are defined as follows:

$$\beta = \ell\frac{a^{\ell+1}}{b^{\ell-1}}F(a,b)+(\ell+1)b^2F(b,b)+\frac{2}{\pi}\varepsilon' ab^2\ell(2\ell+1) \times [F(a,a)F(b,b)-F(a,b)F(b,a)], \quad (7)$$

$$\gamma = \frac{\pi}{2}\frac{\ell(\ell+1)}{2\ell+1}\left[\left(\frac{a}{b}\right)^{2\ell+1}-1\right]-\varepsilon' a\ell^2F(a,a) - \varepsilon'\ell(\ell+1)\frac{a^{\ell+1}}{b^\ell}F(b,a), \quad (8)$$

and the function $F(x,y)$ is defined in the form of an integral [12,14]:

$$F(x,y) = \int_0^\infty \frac{j_\ell(kx)j_\ell(ky)}{\varepsilon(k,\omega)}\mathrm{d}k, \quad (9)$$

where j_ℓ is the spherical Bessel function of order ℓ. In the limit $\varepsilon(k,\omega) \to \varepsilon(\omega)$ in (9), Eq. (6) reduces to the result shown in Eq. (2). In the following, we shall use the simple hydrodynamic model for $\varepsilon(k,\omega)$, in which case Eq. (9) can be obtained in analytical form [14].

3. Results and discussion

We have performed some numerical studies of the enhancement ratio in Eq. (4) for a silver nanoshell using the parameters given in Ref. [14].

Fig. 1 shows the frequency spectrum of the enhancement ratio as a function of scattering frequency for a molecule at $d = 1$ nm for two Ag nanoshells of the same size but different thickness, with a glass core. The following features are clearly noted: (1) the plasmonic resonance is "split" into the antisymmetric (higher frequency ω_+) and symmetric (lower frequency ω_-) modes [14] relative to that of a sphere [15], with more pronounce enhancement at the ω_- mode; (2) the nonlocal (NL) effect will lead to slightly blue-shifted peak in the resonances; as well as (3) significant decrease in enhancement for the thinner shell at low frequencies. All these are consistent with the previous observations from a study of light scattering as well as molecular fluorescence from these nanoshells [14].

Fig. 2 plots a series of spectral enhancement curves for a fixed outer shell radius ($b = 10$ nm) with various values of the inner radius (a) tending to zero (i.e. the metal sphere limit) for both the local and nonlocal theories. The most interesting result to be noted is that, except for the ultra-thin ones, thinner shells in general do yield larger enhancement *at low (IR) frequencies*, although the maximum possible enhancement at the plasmon peak is still greatest for the case of a metal particle. This reconfirms the previous claim of Halas et al. [2,6,9] that shells indeed act as better enhancers at *low (IR) frequencies*. Furthermore, the NL effects again lead to slightly diminished enhancements and blue-shifted plasmon peaks, as already mentioned above. Fig. 3 shows the distance dependence of the

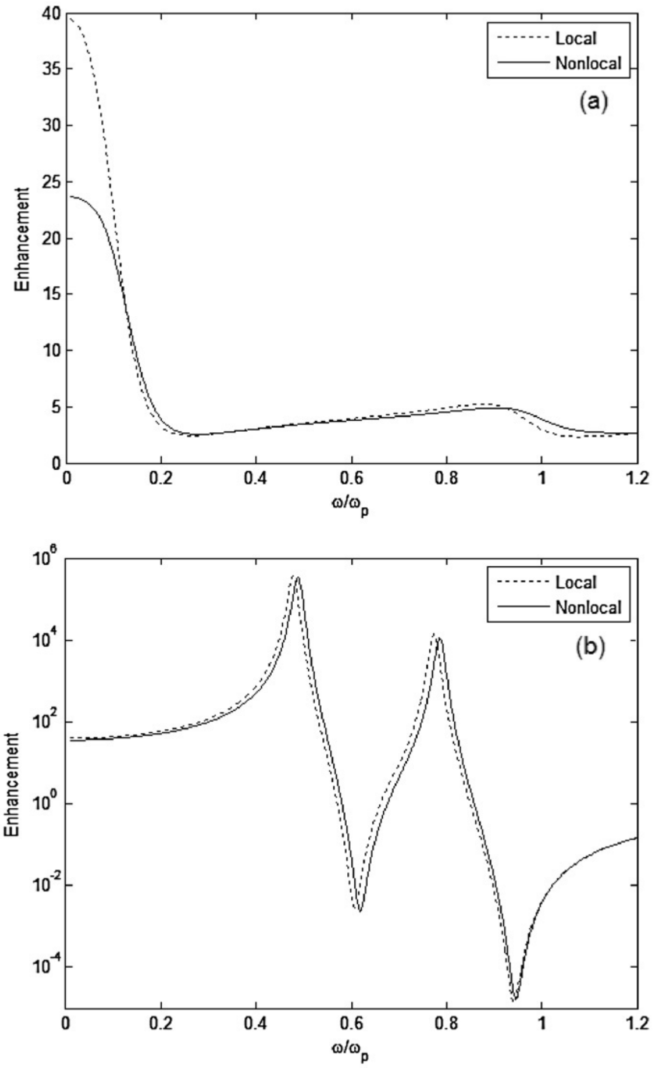

Fig. 1. Enhancement ratio as a function of normalized plasmon frequency for a glass core–silver shell of outer radius 10 nm and inner radius of 9.5 nm (a) and 5 nm (b). The molecule–surface distance is 1 nm.

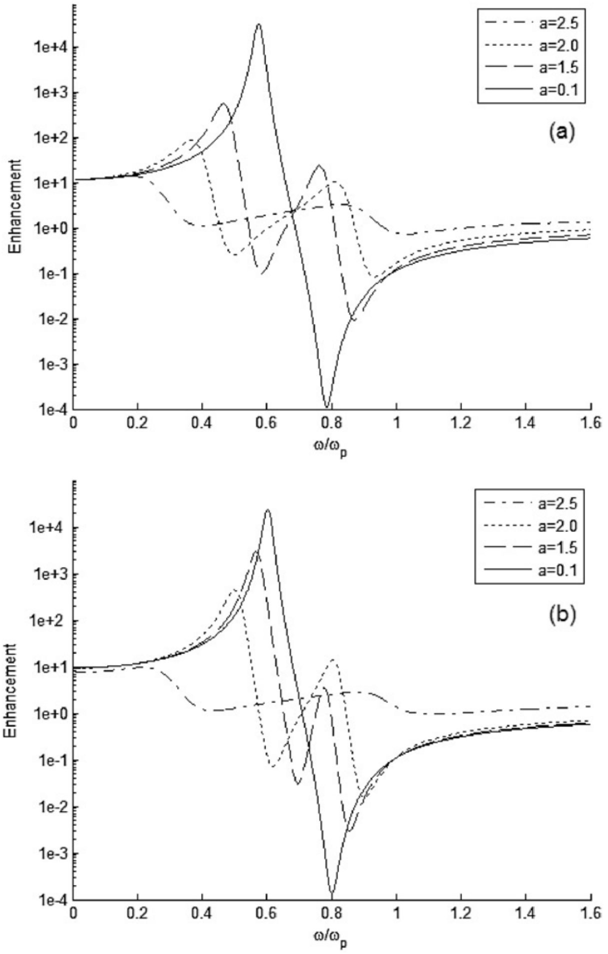

Fig. 2. Local (a) and nonlocal (b) frequency response of the enhancement ratio for a glass core–silver shell with outer radius of 10 nm and various values of the inner radius. The molecule–surface distance is 1 nm.

SERS enhancement for two Ag/glass nanoshells of different sizes and thickness, at scattering frequencies fixed close to the respective symmetric resonance mode (ω_-). It is clear that the NL effects are most pronounced for molecules at close distances from the nanoshell, as well as for small and/or thin shells. For example, the NL effects lead to a decrease of enhancement by ∼40% for the 10 nm/9.5 nm nanoshell at $d \sim 0.5$ nm, and by ∼25% for the 50 nm/30 nm nanoshell at about the same value of d.

Fig. 4 shows a plot of the enhancement as a function of the nanoshell thickness for a shell of outer radius fixed at $b = 10$ nm, at a low frequency close to ω_-. It is interesting to note that while the local theory still shows the presence of an optimal thickness (for a maximum enhancement) for such a small shell, the nonlocal effect makes this disappear. Hence experimentally verifying the *absence* of such an optimal thickness for very small nanoshells will lead to a confirmation of these NL effects. In addition, it is seen that while the NL effects are most notable within a certain range of small thickness values (∼0.5–3.0 nm), the difference between the local and NL results saturates asymptotically towards the results for a solid metal particle [15].

Finally, we compare the case of a Ag/glass nanoshell with that of a hollow Ag shell. Fig. 5 plots the spectral enhancement ratio for each shell according to both the local and nonlocal theories. It is clear that the hollow shell will lead to greater possible enhancements at ω_- for both cases (local and nonlocal), with the nonlocal theory again leading to slightly lower enhancements with blue-shifted plasmon peaks. This can be understood in terms of the symmetric nature of the plasmonic motion for the ω_- modes, for which the hollow shell will provide the most efficient coupling between the "cavity" and "shell" modes due to the symmetric "dielectric environments" at both the outside and inside of the metal shell. This mechanism will not work for the antisymmetric mode, as can be seen from the high-frequency results in the figure, which show a much smaller enhancement for the hollow case.

4. Conclusion

In this work, we have studied the enhanced Raman scattering from a molecule in the vicinity of a metallic nanoshell of

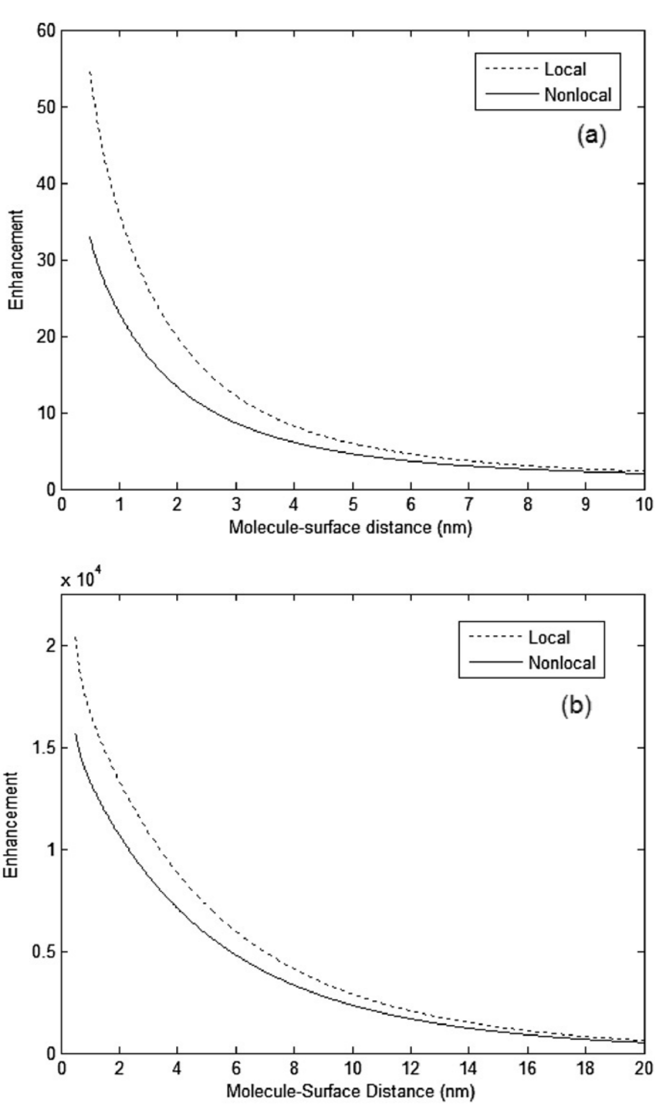

Fig. 3. Enhancement as a function of molecule–surface distance for a glass core–silver shell. In (a), the outer radius is 10 nm and the inner radius is 9.5 nm, with $\omega = 0.05\omega_p$. In (b) the outer radius is 50 nm and the inner radius is 30 nm, with $\omega = 0.4\omega_p$.

ultra-small dimensions. While previous theoretical modeling has been mainly limited to the macroscopic electrodynamic Mie theory, which works well for larger shells of dimensions in the order of several tens of nanometers, we have applied nonlocal electrodynamics to account for possible quantum effects in the optical response of ultra-small nanoshells of dimensions <10 nm. In this approach, we have found that such nonlocal optical effects can be significant for molecules very close to the shell, and for shells of small dimensions and/or thickness. In particular, we predict that the experimental observation of the disappearance of an optimal shell thickness for the maximum SERS signal from small (<10 nm) metallic nanoshells will be a confirmation of these nonlocal effects. In addition, we have demonstrated that, at low (IR) frequencies near the symmetric plasmonic resonance of most nanoshells, the SERS enhancement will in general be greater than that from a corresponding metallic sphere of the same size. This phenomenon is not affected by the nonlocal effects and

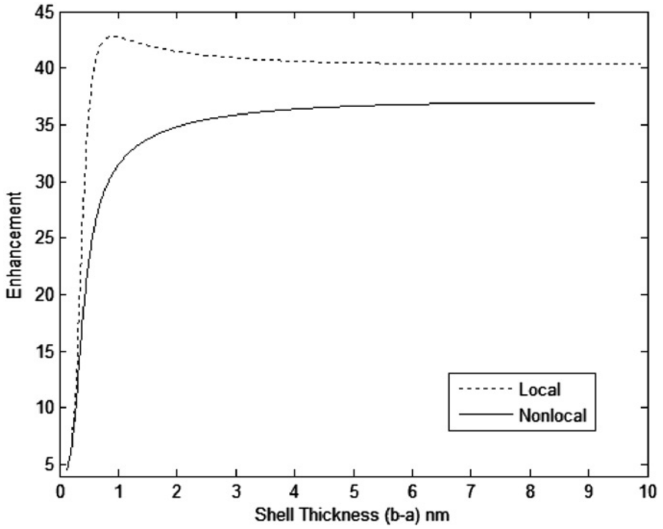

Fig. 4. Local and nonlocal calculations for the enhancement ratio as a function of shell thickness for a glass core shell of outer radius 10 nm, $\omega = 0.05\omega_p$, and at a molecule–surface distance of 1 nm.

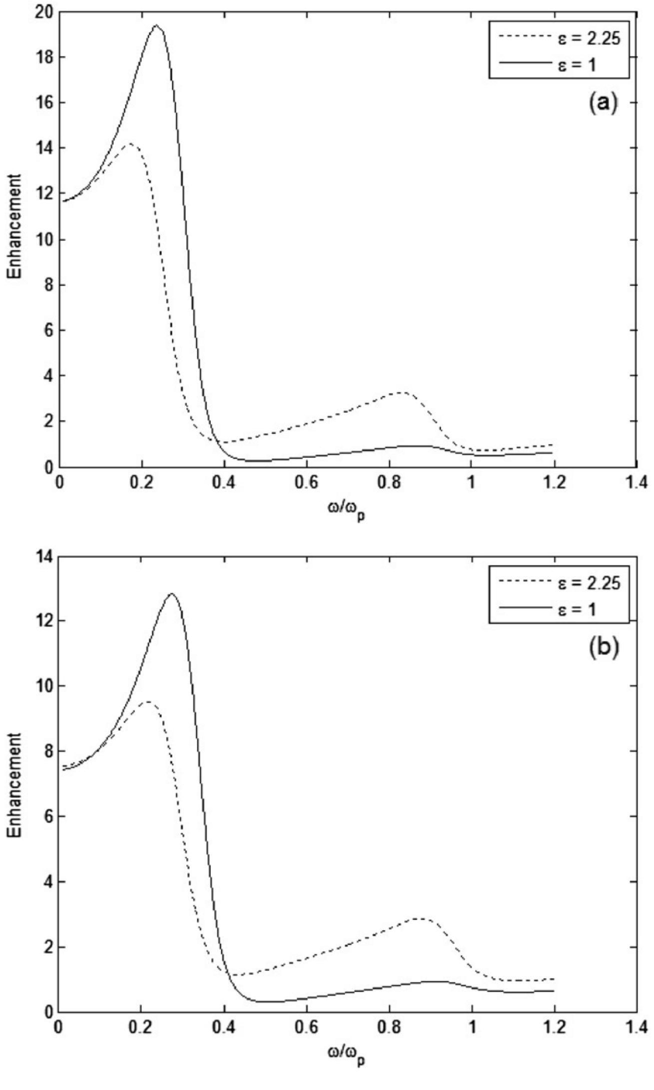

Fig. 5. Local (a) and nonlocal (b) response for the enhancement ratio for shell with a glass core and a hollow shell. The molecule–surface distance is 1 nm.

substantiates the previous conclusions by other researchers [2,6,9].

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